AFRL-OSR-VA-TR-2013-0597

PLEXCITONICS - COUPLED PLASMON-EXCITON SYSTEMS WITH TAILORABLE PROPERTIES

NAOMI HALAS

WILLIAM MARSH RICE UNIVERSITY

11/19/2013
Final Report

AIR FORCE RESEARCH LABORATORY
AF OFFICE OF SCIENTIFIC RESEARCH (AFOSR)/RSA
ARLINGTON, VIRGINIA 22203
AIR FORCE MATERIEL COMMAND

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
11/14/2013	FINAL	8/15/2010/8/14/2013

4. TITLE AND SUBTITLE

Plexitonics:Coupled and plasmon-exciton systems with tailorable properties

5a. CONTRACT NUMBER

5b. GRANT NUMBER

FA9550-10-1-0469

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Lal,Surbhi

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

William Marsh Rice University
6100 Main Street
Houston TX 77005

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFRL

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This project focuses on the interactions between plasmon-resonant- "plasmonic"- materials and structures and molecules, and how the coupling between plasmonic media can modify either molecular- "excitonic" properties. In this three year project we have demonstrated hot electron-induced photodissociation of H2 on Au nanoparticles at room temperature. The Au catalyst nanoparticles are embedded in TiO2 or SiO2 media and the role of the Au plasmon and the embedding media in the dissociation of H2 has been investigated. Single nanoparticle dimer plexitonic structures have been investigated and show the largest Rabi splitting reported. Fano resonant NP clusters have been investigated in efficient four wave mixing and SECARS detection of small and large molecules. In the past year we have also demonstrated efficient steam generation from aqueous nanoparticles solutions without heating the bulk volume of the liquid. Application in ethanol distillation and sanitation have been demonstrated.

15. SUBJECT TERMS

Plasmons, Plexitonic nanostructures, photocatalysis, Fano Resonance, Four wave mixing, SECARS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	UU	5	Surbhi Lal
U	U	U			**19b. TELEPHONE NUMBER** *(include area code)* 713 348 3587

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Plexitonics: Coupled and plasmon-exciton systems with tailorable properties
FA9550-10-1-0469
8-15-2010 to 8-14- 2013

Report abstract:

This project focuses on the interactions between plasmon-resonant- "plasmonic"- materials and structures and molecules, and how the coupling between plasmonic media can modify either molecular- "excitonic" properties. In this three year project we have demonstrated hot electron-induced photodissociation of H2 on Au nanoparticles at room temperature. The AU catalyst nanoparticles are embedded in TiO2 or SiO2 media and the role of the Au plasmon and the embedding media in the dissociation of H2 has been investigated. Single nanoparticle dimer plexitonic structures have been investigated and show the largest Rabi splitting reported. Fano resonant NP clusters have been investigated in efficient four wave mixing and SECARS detection of small and large molecules. In the past year we have also demonstrated efficient steam generation from aqueous nanoparticles solutions without heating the bulk volume of the liquid. Applications in ethanol distillation and sanitation have been demonstrated.

Key Accomplishments:

We have reported the room temperature dissociation of H2 on gold nanoparticles using visible light. Surface plasmons excited in the Au nanoparticle decay into hot electrons with energies between the vacuum level and the work function of the metal. In this transient state, hot electrons can transfer into a Feshbach resonance of an H2 molecule adsorbed on the Au nanoparticle surface, triggering dissociation. We probed this process by detecting the formation of HD molecules from the dissociations of H2 and D2 and investigated the effect of Au nanoparticle size and wavelength of incident light on the rate of HD formation. This work opens a new pathway for controlling chemical reactions on metallic catalysts. This work was the first experimental evidence of room temperature photocatalytic dissociation of H2.

The binding energy and sticking coefficient of H2 on gold is very small and the molecules would not adsorb on a pure gold surface. To increase H2 accommodation, the gold nanoparticles were supported on TiO2. The TiO2 matrix, into which H2 diffuses, provides a passive function, ensuring that the H2 molecules remain for a sufficiently long time near the Au surface to allow for hot electron transfer into an antibonding dissociative molecular resonance. We show that hot electrons, created from plasmon decay, can transfer into a closed shell H2 molecule and induce dissociation. This effect provides a path for the optical control of chemical reactions. By tuning the plasmon resonances of metallic nanoparticles appropriately, it may be possible to populate specific electronic states of molecules adsorbed on the nanoparticle surface. This state-selective population of adsorbate resonances could be exploited to prepare reactants in specific states on nanoparticle surfaces, thus enabling an unprecedented, all-optical control of chemical reactions. (Mukherjee et al. Nanoletters, 2013)

In the past year we have investigated the hot electron-induced photodissociation of H2 on small Au nanoparticles supported on SiO2. The rate of dissociation of H2 was found to be almost two orders of

magnitude higher than that observed on equivalently prepared Au nanoparticles on TiO2. The rate of H2 dissociation was found to be linearly dependent on illumination intensity, with the wavelength of incident light dependent upon the plasmon resonance of the Au nanoparticle. This result provides strong additional support for this photocatalytic system. In comparison to our previous study of H2 dissociation on Au NPs on TiO2, the reaction rate in the presence of SiO2 is enhanced by almost two orders of magnitude. This result strongly supports the proposed mechanism that hot electrons generated by plasmon decay transfer to the H2 molecules, substantially reducing the barrier for H2 dissociation. The result supports our earlier conclusion that the dielectric support plays a passive role in this reaction process. A plausible explanation for the substantially larger dissociation rate in the presence of an SiO2 relative to TiO2 nanoparticle support is the presence of a Schottky barrier at the AuNP/TiO2 surface, which may facilitate hot electron transfer into the TiO2 matrix creating a competing channel for hot electron H2 dissociation. We also observe the possible oxidation of SiO2 to SiO that appears to be photocatalytically mediated by the hot electron H2 dissociation process, which may prove to provide a low temperature photoinduced reaction pathway for this typically high temperature process. (Mukherjee et al., manuscript to be submitted)

Strong coupling between resonantly matched localized surface plasmons and molecular excitons results in the formation of new hybridized energy states called plexcitons. Understanding the nature and tunability of these hybrid nanostructures is important for both fundamental studies and the development of new applications. We investigate the interactions between J-aggregate excitons and single plasmonic dimers and report for the first time a unique strong coupling regime in individual plexcitonic nanostructures. Dark-field scattering measurements and finite-difference time-domain simulations of the hybrid nanostructures show strong plexcitonic coupling mediated by the near-field inside each dimer gap, which can be actively controlled by rotating the polarization of the optical excitation. The plexciton dispersion curves, obtained from coupled harmonic oscillator models, show anticrossing behavior at the exciton transition energy and giant Rabi splitting ranging between 230 and 400 meV. These energies are, to the best of our knowledge, the largest obtained on individual hybrid nanostructures. Further engineering of these hybrid nanostructures, by introducing symmetry breaking for instance, can lead to comparably larger near-field enhancements and introduce the possibility of coupling excitons to higher order dark LSP modes. The quantitative investigation of plexciton formation we reported here with an unprecedented control in the single particle regime opens up a new way to promising nanoscale application at optical frequencies. (Schlather et al. Nanoletters 2013)

Plasmonic nanoclusters, an ordered assembly of coupled metallic nanoparticles, support unique spectral features known as Fano resonances (FRs) due to the coupling between their subradiant and superradiant plasmon modes. Within the Fano resonance, absorption is significantly enhanced, giving rise to highly localized, intense near fields with the potential to enhance nonlinear optical processes. We have investigated a 13 nanodisk cluster structure supporting the coherent oscillation of two distinct Fano resonances within an individual plasmonic nanocluster. When both FRs of the nanocluster are excited simultaneously (by two coherent beams), the plasmons oscillate in a mixed frequency “coherent state.” In this mode, the charge oscillation of the central disk switches rapidly between an in-phase and out-of phase motion with respect to the outer ring, in each case corresponding to the oscillatory

behavior of one of the FRs. For the coherent state, enhanced local fields at multiple resonant frequencies overlap not only in time but also in space, contributing to the nonlinear optical wave mixing. We show how this coherence enhances the optical four-wave mixing process in comparison with other double resonant plasmonic clusters that lack this property. A model that explains the observed four-wave mixing features is proposed, which is generally applicable to any third-order process in plasmonic nanostructures. With a larger effective susceptibility χ (3) relative to existing nonlinear optical materials, this coherent double-resonant nanocluster offers a strategy for designing high-performance third order nonlinear optical media. (Yu Zhang et al. PNAS 2013)

Coherent anti-Stokes Raman scattering (CARS) is a specific FWM process and a third-order coherent nonlinear Raman scattering process involving the pump and Stokes fields at frequencies ω_P and ω_S ($\omega_S < \omega_P$), respectively. Both fields interact coherently through the third-order susceptiblity $\chi^{(3)}$ of the molecule-bond and generate a blue-shifted signal at the anti-Stokes frequency $\omega_{AS} = 2\omega_P - \omega_S$ with intensity

$$I_{CARS} \propto |\chi^{(3)}|^2 I_P^2 I_S.$$

When the frequency difference between the pump and Stokes ($\omega_P - \omega_S$) coincides with a Raman band, the CARS signal is resonantly enhanced as a scattering peak. Although CARS is more sensitive than spontaneous Raman due to its higher order power dependence, its sensitivity is still not enough for examining a small numbers of molecules. We have designed a plasmonic quadumer nanocluster of gold disks that support a Fano resonance (FR). The FR is spatially confined hot spot in the central gap of the asymmetric quadrumer, and is resonant with all three frequencies (ω_P, ω_S and ω_{AS}). We have measured the surface enhanced CARS (SECARS) signal from small molecules like *p-mercapto aniline,* and larger biologically significant molecules adenine and benzocaine. (Yu Zhang et al., manuscript to be submitted).

Solar illumination of broadly absorbing metal or carbon nanoparticles dispersed in a liquid produces vapor without the requirement of heating the fluid volume. When particles are dispersed in water at ambient temperature, energy is directed primarily to vaporization of water into steam, with a much smaller fraction resulting in heating of the fluid. These phenomena can also enable important compact solar applications such as sterilization of waste and surgical instruments in resource-poor locations. Using absorptive nanoparticles dispersed in water, we demonstrate efficient direct steam generation using solar illumination. A thermodynamic analysis shows that 80% of the absorbed sunlight is converted into water vapor and only 20% of the absorbed light energy is converted into heating of the surrounding liquid. In an application to ethanol distillation, we show that the distillate contains a higher percentage of ethanol than what is predicted by the water ethanol azeotrope. These findings cast doubts on the conventional macroscopic models for thermal transport between nanoparticles and their environment and suggest that significant thermal barriers may be present at the nanoparticle liquidvapor bubble interfaces. Most importantly, our findings open up a wide range of novel compact solar energy applications such as distillation, desalination, and sterilization and sanitation applications in resource-poor locations.(Neumann et al. ACS Nano 2013)

Publications:

1. Shaunak Mukherjee*, Linan Zhou*, Amanda M. Goodman, Nicolas Large, Ciceron Ayala Orozco, Yu Zhang, Peter Nordlander, Naomi J. Halas, "Hot Electron Induced Dissociation of H2 on Au nanoparticles supported on SiO_2" To be submitted

2. Yu Zhang, Yu-Rong Zhen, Oara Neumann, Jared K. Day, Peter Nordlander and Naomi J. Halas, "Coherent anti-Stokes Raman scattering enhanced by a Fano resonant plasmonic nanocluster with single nonresonant molecule sensitivity". To be submitted

3. Oara Neumann, Curtis Ferontic, Albert D. Neumann, Anjie Dongd, Kevin Schelld, Benjamin Lue, Eric Kime, Mary Quinne, Shea Thompson, Nathaniel Grady, Peter Nordlander, Maria Odene, and Naomi J. Halas. Compact solar autoclave based on steam generation using broadband light-harvesting nanoparticles. *P. Natl. Acad. Sci. USA* **2013,** *110,* 11677-11681.

4. Andrea E. Schlather*, Nicolas Large*, Alexander S. Urban, Peter Nordlander, and Naomi J. Halas. Near-Field Mediated Plexcitonic Coupling and Giant Rabi Splitting in Individual Metallic Dimers. *Nano Lett.* **2013**, *13*, 3281–3286.

5. Yu Zhang, Fangfang Wen, Yu-Rong Zhen, Peter Nordlander, and Naomi J. Halas. Coherent Fano resonances in a plasmonic nanocluster enhance optical four-wave mixing. *P. Natl. Acad. Sci. USA.* **2013,** *110,* 9215-9219.

6. Shaunak Mukherjee, Florian Libisch, Nicolas Large, Oara Neumann, Lisa V. Brown, Jin Cheng, J. Britt Lassiter, Emily A. Carter, Peter Nordlander, and Naomi J. Halas. Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H_2 on Au. *Nano Lett.* **2013,** *13,* 240-247.

7. Oara Neumann, Alex Urban, Jared Day, Surbhi Lal, Peter Nordlander, and Naomi J. Halas. Solar Vapor Generation Enabled by Nanoparticles. *ACS Nano* **2013,** *7,* 42-49.

8. Na Liu, Shaunak Mukherjee, Kui Bao, Lisa Brown, Jens Dorfmuller, Peter Nordlander, and Naomi J. Halas, "Magnetic plasmon formation and propagation in artificial aromatic molecules", Nano Letters 12, 364-9 (2012).

9. Brooke Hester, Gretchen K. Campbell, Carlos Lopez Mariscal, Carly Levin Filgueira, Ryan Huschka, Naomi J. Halas, and Kristian Helmerson, "Tunable optical tweezers for wavelength-dependent measurements", Reviews of Scientific Instruments 83, 043114 (2012).

10. Jian Ye, Fangfang Wen, Heidar Sobhani, J. Britt Lassiter, Pol Van Dorpe, P. Nordlander, and N. J. Halas, "Plasmonic nanoclusters: near field properties of the Fano resonance interrogated with Surface Enhanced Raman Scattering", Nano Letters 12, 1660-1667 (2012).

11. Na Liu, Shaunak Mukherjee, Kui Bao, Yang Li, Lisa V. Brown, Peter Nordlander, and Naomi J. Halas, "Manipulating magnetic plasmon propagation in metallic nanocluster networks", ACS Nano **6**, 5482–5488(2012).

12. Yu Zhang and N. J. Halas, "Three-dimensional nanostructures as highly efficient generators of second harmonic light", Nano Letters 11, 5519-5523 (2011).

13. Aoune Barhoumi and N. J. Halas, “Detecting epigenetic modifications of DNA using SERS”, Journal of Physical Chemistry Letters 2, 3118-3123 (2011).

14. R. Huschka, J. Zuloaga, M. W. Knight, L. Brown, P. Nordlander and N. J. Halas, “Plasmon-assisted DNA release from nanoshells and nanorods”, Journal of the American Chemical Society 133, 12247-12255 (2011).

Student Thesis:

1. Shaunak Mukherjee: Engineered Plasmonic Nanostructures: Fano Resonance Response, Magnetic Plasmon Resonance for Waveguiding and Hot Electron Induced Photochemistry

2. N. Tumasang: Optical Properties of Strongly Coupled Plasmon-Exciton Hybrid Nanostructures.

3. Ryan Huschka: Light-Triggered Release of DNA from Plasmon-Resonant Nanoparticles.